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<p>(21) International Application Number: PCT/IB95/00609 (22) International Filing Date: 4 August 1995 (04.08.95) (71) Applicant: INTERNATIONAL BUSINESS MACHINES CORPORATION [US/US]; Old Orchard Road, Armonk, NY 10504 (US). (72) Inventors: BIEBUYCK, Hans, Andre; Mythenstrasse 8, CH-8800 Thalwil (CH). MICHEL, Bruno; Obstgartenweg 13, CH-8136 Gattikon (CH). (74) Agent: BARTH, Carl, Otto; International Business Machines Corporation, Säumerstrasse 4, CH-8803 Rüschlikon (CH).</p>		<p>(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>
<p>(54) Title: STAMP FOR A LITHOGRAPHIC PROCESS</p> <div data-bbox="289 1192 1234 1423" data-label="Image"></div> <p>(57) Abstract</p> <p>A hybrid stamp structure for lithographic processing of features below 1 micron is described, comprising an deformable layer (14) for accommodating unevenness of the surface of a substrate and of the stamp structure itself, and a patterned layer (12) in which a lithographic pattern is engraved. The stamp structure is further enhanced by comprising a third layer (16), which acts as rigid support for the stamp, thus preventing an undesired deformation of the stamp under load.</p>		

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DESCRIPTION**Stamp for a Lithographic Process**

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The present invention is directed generally toward a lithographic process. More particularly, it relates to an elastomeric stamp for use in such a lithographic process.

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BACKGROUND OF THE INVENTION

Since the emergence of integrated circuits (ICs) and micromechanical devices, optical lithography has been crucial for the purpose of their mass production: Its convenience, parallel operation and resolution has created a huge market. Fabrication of devices with ever smaller dimensions, necessary to satisfy the increasing demands of storage and computation, becomes increasingly problematic with visible light as processes steadily reaching fundamental limits, predominantly set by diffraction. This realization triggered intense research in UV, X-ray, e-beam, and Scanning Probe (SP) lithography. These methods deliver high resolution with varying success and their economics remain, at best, uncertain. Reasons for these uncertainties include limitations due to wavelength dependent phenomena, the slow writing speeds of e-beam and SP lithographies, and challenges in finding appropriate resists.

A separate and related limitation of current lithographies is the complexity of processes required for pattern transfer; lithography today relies on transfer of material from the liquid or gas phase using masks to protect certain regions of the substrate so that devices are filled in more than assembled.

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1 An alternative approach to lithography has been published by A. Kumar and
G.M. Whitesides in: Appl. Phys. Lett. 63 (14), 4 October 1993, pp. 2002-2004.
In this process, referred to as stamp lithography, stamps are fabricated by
casting poly(dimethylsiloxane) (PDMS) on a master with a negative of the
5 desired pattern. The PDMS stamp is peeled away from the master after
curing and exposed to an "ink" transferred to the substrate by transient
contact with the stamp. The elastomeric nature of the PDMS allows contact
even on rough or curved surfaces. According to this method, features
between 1 and 100 microns are achieved. For larger stamps and larger
10 features (1 cm to 200 microns), the pattern is directly etched into the stamp
by conventional UV lithography using a mild soap solution for dissolving
those regions previously exposed to the UV light. When applying this
method to lithography with submicron features, it was found that no
reproducible results necessary for mass-production of ICs were attainable
15 with a type of stamp as propagated by Kumar et al. A major limitation of this
method of pattern transfer is the elastomer used as carrier of the pattern.
This material is deformable so that repeated, accurate transfer of the pattern
to the substrate with high resolution, as necessary for practical lithography,
is not possible.

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Therefore, it is seen as an object of the invention to improve the method
described by Kumar et al. such that stamp lithography can compete with the
current state-of-the-art lithography. Particularly, features of 0.1 to 1 microns
width should be achievable in a reproducible manner, suitable also for
25 covering conventional wafer sizes.

SUMMARY OF THE INVENTION

30 The object of the invention is achieved by a stamp as set forth in the
appended claims. The new composite stamp avoids the limitations of the
prior art stamp. Using the new stamp, feature sizes or a "design rule" of
below one micron can be achieved in a reproducible manner. Due to its

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1 novel structure it can be optimized for matching all important properties,
i.e., rigidity, conformal contact, and accurate pattern transfer,
simultaneously.

5 It is seen as an important feature of the invention that the stamp comprises
an deformable or elastic layer for conformal contact, accommodating the
fluctuations of the thickness of the substrate and impurities on its surface,
and a second (patterned) layer, which carries the desired pattern. This
layer is preferably made of a material having a Young's modulus in the
10 range of 10^4 to 10^7 , more preferably of $0.25 \cdot 10^6$ to $5 \cdot 10^6$ dyne/cm². Material
having this property can be poly(butyldiene), poly(dimethylsiloxane),
poly(acrylamide), poly(butylstyrene) and co-polymers of these types. It is
desirable to optimize the properties of the elastic layer such as to control
the desired amount of flexibility.

15

A stamp made in accordance with the invention has several advantages
over the known uniform elastomeric stamp. The materials of both layer can
be optimized to a large extent independently of each other. Thus it is
desirable to have a patterned layer to which submicron features can readily
20 be written by a lithographic process. The patterned layer should also easily
adhere to or absorb a specific "ink" material. It is further desirable to
produce the patterned layer from a preferably non-deformable material
which accurately preserves the pattern features even after repetitive
application in the lithographic process. The patterned layer can be made of
25 an material with a high Young's modulus, preferably above 10^6 dyne/cm².
Suitable materials could be organic, such as poly(styrene) or
poly(methylmethacrylate), metallic, such as gold, platinum, palladium,
nickel, titanium and oxides thereof, or inorganic insulators like alumina,
silicon, silica, or perovskites, depending on the desired properties and
30 application.

1 In a preferred embodiment of the invention, the elastomeric layer is
mounted onto a rigid support structure being even within a tolerance of less
than 10 microns, preferably in the range of 1 micron to 1 nm. A preferred
support material has a thermal expansion coefficient close to the one of the
5 substrate material. The support is preferably chosen from a group
consisting of glass, quartz glass, rigid plastics material, or the substrate or
wafer material, e.g. silicon. When mounted on a support structure, the
elastic layer itself can be thin. Its thickness lies preferably in a range of 10
to 1000 microns. In this range of thickness, any deformation can be
10 accommodated by the elastic layer, while the features of the pattern
maintain their dimensions even when the stamp is pressed during the
lithographic process. When protruding self-alignment means are used, as
are described below, the thickness of the elastic layer may preferably be
chosen from a range of 10 to 10000 microns. Obviously, a support structure
15 as described above can also be advantageously applied to the known
one-layer stamps as described by Kumar et al.

In a further preferred embodiment, the stamp comprises means for
achieving a self-alignment. The means could either comprise key-and-lock
20 type topological features, e.g. cone- or pyramid-shaped protrusions and
holes, which after a sufficiently accurate pre-positioning by stepping drives
guide the stamp into the desired final position. A preferred means for
self-aligning the stamp and the substrate however exploits surface tension
gradients provided on the surface of the stamp and/or substrate. These
25 gradients are, for example, achieved by distributing pads on the surface of
substrate and stamp, said pads being characterized by a modified surface
providing a higher affinity to a liquid, e.g. oil or water.

These and other novel features believed characteristic of the invention are
30 set forth in the appended claims. The invention itself however, as well as
a preferred mode of use, and further objects and advantageous thereof, will
best be understood by reference to the following detailed description of

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1 illustrative embodiments when read in conjunction with the accompanying drawings.

5

DESCRIPTION OF THE DRAWINGS

The invention is described in detail below with reference to the following drawings:

10 **FIG. 1A - 1D** illustrate basic steps of a first method for producing a stamp according to the invention.

FIG. 2A - 2D illustrate basic steps of a second method for producing a stamp according to the invention.

15

FIG. 3 illustrates a key-and-lock type means for self-alignment of a stamp and a substrate.

20 **Figs. 4 A,B** illustrates means for self-alignment of a stamp and a substrate based on a surface tension gradient.

Figs. 5 - 7 illustrates the basic steps of preparing a stamp and a substrate for stamp lithography.

25 **FIG. 8** illustrates the use of a new stamp in accordance with the invention in a lithographic process.

MODE(S) FOR CARRYING OUT THE INVENTION

30

A first example of the invention is now described, referring to figures 1A to 1D. The process starts with a silicon wafer 10, which provides a very flat surface. The surface is coated with a thin layer 11 of perfluorinated silane.

1 The perfluorinated silane prevents an adhesion or bonding of the following
layers to the silicon surface. Next, a layer of a brittle material capable of
accurately holding a pattern is deposited onto layer 11. The brittle material
is either poly(methylenmethacrylate)(PMMA), which is deposited by
5 spincoating or polysilicon which is deposited by chemical vapor deposition.
Both deposition methods are well known in the art. The layer thickness is
chosen in dependence of the average features size, the so-called "design
point" in a ratio of approximately 1:1. The layer 12 is structured by
conventional UV lithography, or alternatively by e- beam lithography. Spacer
10 elements 13 are positioned on the wafer 10. Into the volume defined by the
spacer elements, pre-polymers of poly(dimethylsiloxane)(PDMS) are cast to
form, after a curing process, an elastic layer 14 over the patterned PMMA or
polysilicon 12. A second silicon wafer 16 is lowered onto the spacer
elements, squeezing any surplus amount of PDMS through gaps between
15 the spacer elements. This second silicon waver is pre-treated with an olefin
terminated silane which provides a glue-like layer 15 to bond to the PDMS.
By lifting the assembly, the lower layer 10 of silicon is separated from the
rest. Thereafter, the patterned layer of PMMA or polysilicon is developed
by dissolving or etching the exposed areas, resulting in a composite stamp
20 structure as illustrated by Fig. 1D.

An additional layer 17 can be introduced between the patterned PMMA
layer 12 and the deformable layer 14 to provide an additional support for
the pattern after its development. In the example as illustrated by Fig. 1E,
25 this intermediate layer consists of PMMA. However this layer can be
replaced by a layer of indium tin oxide (ITO), an electrically conductive
material. This additional layer besides providing an enhanced stability of the
pattern (and electrical conductivity) also prevents the elastic material of
layer 14 from penetrating through the openings of the patterned layer 12.

30

A second method for producing a composite stamp is illustrated by Figs. 2A
- 2D. First, a master substrate 20 is provided by any conventional
lithography method (or by the stamping lithography describe herein). The

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1 master pattern is treated with perfluorinated silane 21 as a separating agent.
Thereafter, a layer 22 of PMMA is spincoated onto the assembly. The
following steps (Figs. 2C, 2D) correspond to those of the previous example.
By lifting the assembly, the stamp and the master are separated, leaving the
5 master 20 for further replication of the stamp.

Referring now to Fig. 3, a first self-alignment means on substrate 30 and
stamp 31 is shown, comprising of wedge-shaped protrusions 311 of PMMA
exceeding the features of the lithographic pattern 312. The protrusions 311
10 fit exactly into corresponding recesses 301 of the substrate. This can be
achieved by employing the same alignment stamp when producing the
recesses 301 in the substrate and in the master from which the stamp is
replicated. Provided that the substrates are made of the same material and
all etching parameters are equal, the wedges 311 and the recesses 301
15 match exactly. This concept of providing matching marks on the substrate
and on the stamp is described in further detail below.

Whereas in the lock-and-key type of self-alignment the geometrical shape of
the features, e.g. the tilted sidewalls, cause a fine-adjustment of the stamp
20 and the substrate, the following example of self-alignment means, as being
illustrated by Figs. 4A and 4B, is based on the property or tendency of a
liquid to minimize its surface. With hydrophilic pads 401, 411 on the
surfaces of both, the substrate 40 and the stamp 41, together with a
controlled amount of moisture, leading to the formation of small droplets on
25 and between these pads, an efficient self-aligning mechanism is realized: In
case of a small misalignment of the stamp with respect to the substrate, a
sandwiched droplet 420 provides a restoring force back to the regular
shape, thereby moving the stamp into its desired position. The droplet can
be generated in a controlled manner by exposing the pads to a moisturized
30 inert gas (humidified nitrogen). It should be noted that the features of Fig. 4
are as all other figures not drawn to scale. The size of the droplet should be
approximately of the order of the cubic of the design rule.

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1 The efficacy of this method can be increased by depositing a hydrophobic zone 402 around each of the pads 401 or by placing the pads on post-type supports 412 as shown in Fig. 4B. Another advantageous property of the sandwiched droplet 420, also illustrated by Fig. 4B, is its acting as a elastic
5 cushion when pressure is exerted upon the assembly. Thus, the stamp immediately is lifted from the substrate when releasing the exerted pressure by the spring forces of the deformed droplets 420 and/or posts 412.

Self-alignment means should be placed in the vicinity of cleavage lines of
10 the wafer thus ensuring that a minimum of utilizable wafer area is occupied. The lateral dimensions of the self-alignment means again are in the order of the design rule.

The following figures are to illustrate the basic steps of preparing an aligned
15 assembly consisting of a wafer substrate and one or several stamps.

In a first step, an alignment master 50 as shown in Fig. 5 is prepared, which carries recesses 501 at preselected positions, which preferably are located at regions designed to be the cleavage lines of the wafer to be
20 manufactured. Of the alignment master several alignment stamps 61 can be produced as replicas carrying alignment marks 611 (Fig. 6A). To provide hydrophilic pads on a wafer, a replica of the alignment stamp is inked with 16-mercaptohexadecanol acid 612 or, alternatively, with 16-mercaptohexadecanol, which is transferred by stamp contact printing
25 (Fig. 6B) onto a wafer 60 covered with a thin gold film 601, which adheres to the thiol. The uncovered gold film is then removed, exploiting the thiol pad 602 as protective coating. After evaporating another gold film while shielding the neighborhood of the pads by a mask, the wafer is prepared for further processing (Fig. 6C).

30

Referring now to Fig. 7A, a silicon stamp master 70 is shown coated with perfluorinated silane 702. Prior to the lithographic pattern 703, alignment recesses 701 are marked and etched into the silicon using an alignment

1 stamp drawn from the alignment master as shown in Fig. 5. The lithographic
pattern **703**, produced by conventional e-beam lithography, is written using
coordinates relative to the alignment marks **701**. By using the same
alignment stamp for different stamp masters and by positioning the
5 lithographic pattern relatively to the alignment marks, stamps with different
lithographic patterns can be manufactured. These stamps can replace the
masks used in the known lithographic methods. Due to the above described
manufacturing procedure, these stamps are inherently aligned to each
other. By using the same alignment stamp for the wafer, as is described
10 above when referring to Figs. 6A-6C, all such produced stamps can be
placed in a self-aligning fashion onto the wafer.

The stamp master is spincoated with the pattern layer of the composite
stamp **712** (PMMA), shown in Fig. 7B. Before applying the elastic layer **714**
15 (PDMS), the resist within the recesses **701** is exposed, etched away and
replaced by a thin layer of gold **718** (Fig. 7C). Then spacer elements **713** are
installed at the perimeter of the stamp master, and the thus created volume
is filled with the elastomer **714** (Fig. 7D). As described above, a second
silicon plate **716** is applied as supporting layer. After lifting the stamp
20 assembly and trimming of its rim (Fig. 7E), the stamp **71** is dipped into a
solution of carboxyl (COOH) terminated thiols **705** to apply hydrophilic pads
718 to the alignment protrusions **711**. The preparation of the stamp **71** is
completed by wetting the layer **712** with lithographic pattern with the
substance **719** to be transferred to the wafer (Figs. 7F, 7G).

25
For the actual lithographic process, as illustrated by Fig. 8, a moisture
carrying gas is blown over the hydrophilic pads **601** on the surface of the
wafer **60** as prepared in a previous step (Fig. 6C). The stamp **71** is
positioned by known alignment means such that its hydrophilic pads **718** are
30 in approximate juxtaposition of those on the wafer. The final alignment is
then achieved by the surface tension of the droplets **820** sandwiched
between the hydrophilic pads.

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- 1 The lithographic pattern is transferred to the wafer **60** by exerting pressure
on the stamp **71** until the wetted layer **712** touches the surface layer **601** of
the wafer. The substance **719**, which could be a reactant, etchant, protective
coating, etc., is then transferred at all areas of contact.

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CLAIMS

1. Stamp structure for a lithographic process, comprising a deformable layer (14; 24) of a first material for making a conformal contact between
5 the surface of a substrate (30; 40; 60) and of said stamp structure, and a patterned layer (12; 22) of a second material with a lithographic pattern to be transferred to said substrate.
2. The stamp structure of claim 1, further comprising a rigid support (16;
10 26) for preventing an undesired deformation of the deformable layer under a load.
3. The stamp structure of claim 1, further comprising self-aligning means (301, 311; 401, 411, 420) for an accurate relative positioning and/or
15 deformation of the substrate (30; 40) and the stamp structure (31; 41) during the lithographic process.
4. The stamp structure of claim 3, wherein the self-aligning means comprises protruding elements (311) and corresponding recess
20 elements (301), preferably with tilted sidewalls.
5. The stamp structure of claim 3, wherein the self-aligning means comprises a surface tension gradient.
- 25 6. The stamp structure of claim 5, wherein surface tension gradient is achieved by pads (401, 411) having a higher affinity to a liquid than their surrounding areas.
7. Use of a stamp structure in accordance with claim 1 for submicron
30 lithography.
8. Lithographic process comprising the steps of

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1 - preparing a stamp structure comprising a deformable layer (14; 24;
714) of a first material for making a conformal contact between the
surface of a substrate (30; 40; 60) and of said stamp structure, and a
patterned layer (12; 22; 712) of a second material with a lithographic
5 pattern to be transferred to said substrate;

- applying a substance (719) to said patterned layer; and

10 - bringing said patterned layer into a conformal contact with said
surface of said substrate.

9. The lithographic process of claim 8, further comprising the steps of

15 - preparing a master alignment stamp (60) carrying alignment marks
(611); and

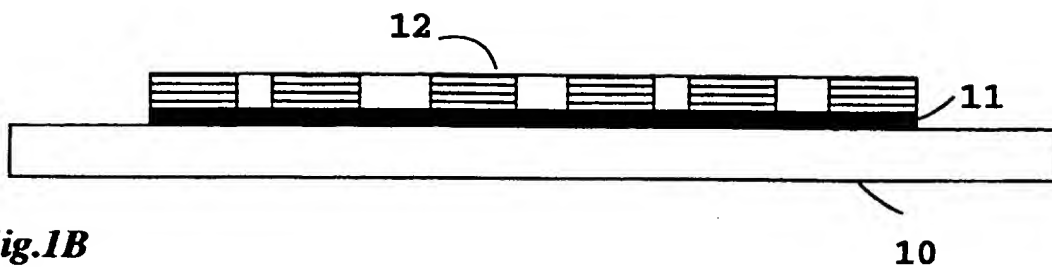
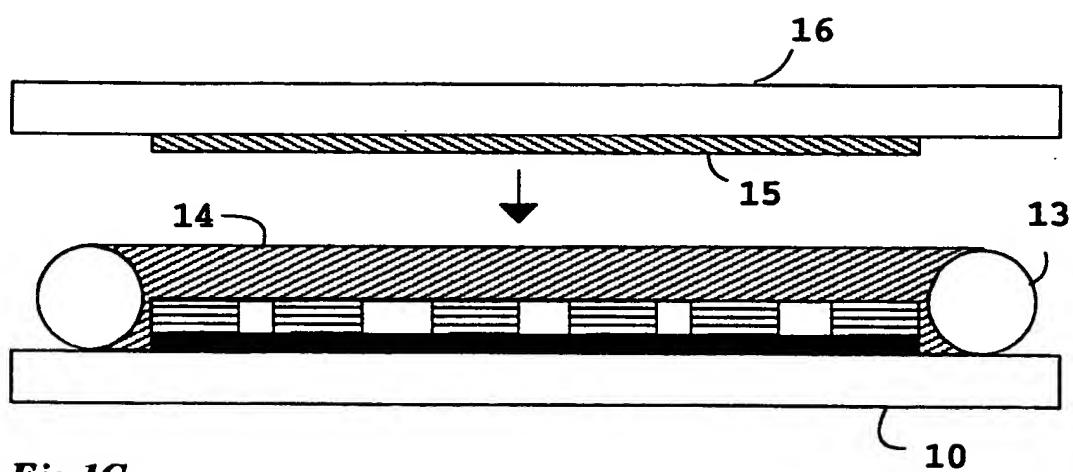
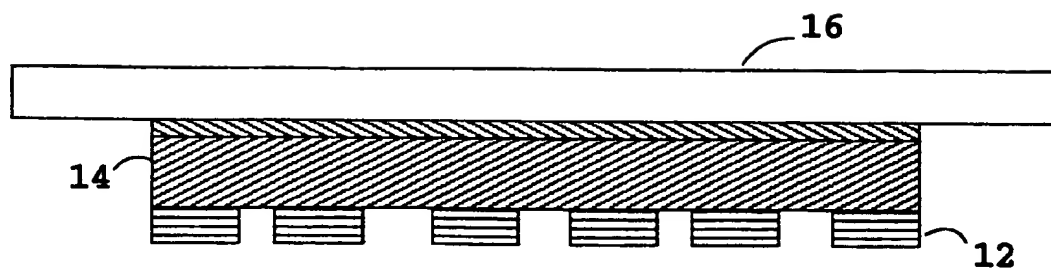
20 - using said alignment master for reproducing self-alignment means
(602; 718) on the substrate and the patterned layer at precisely
corresponding positions.

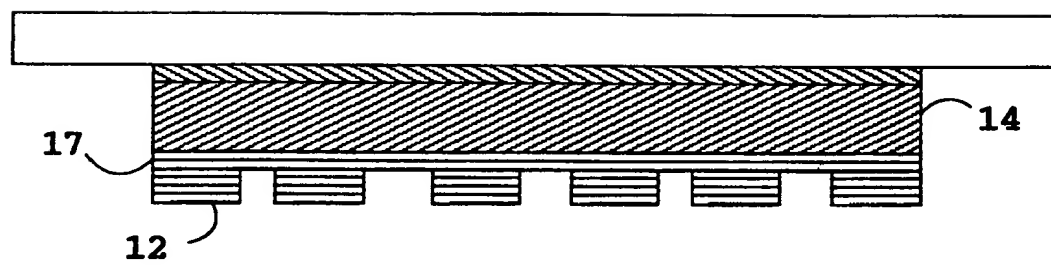
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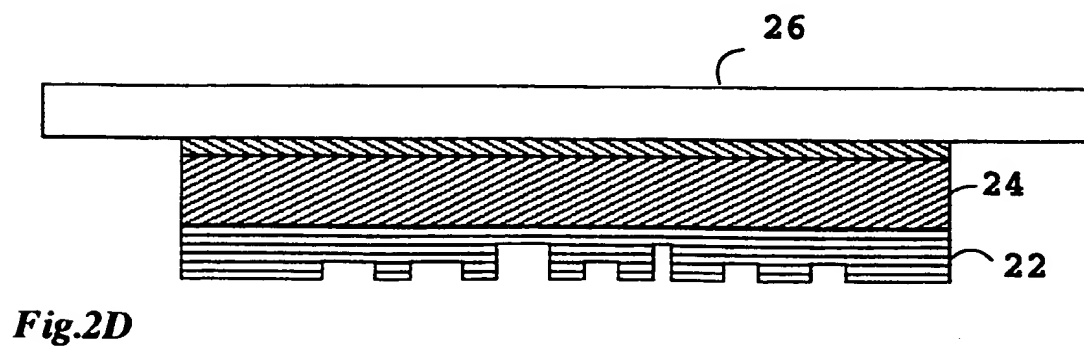
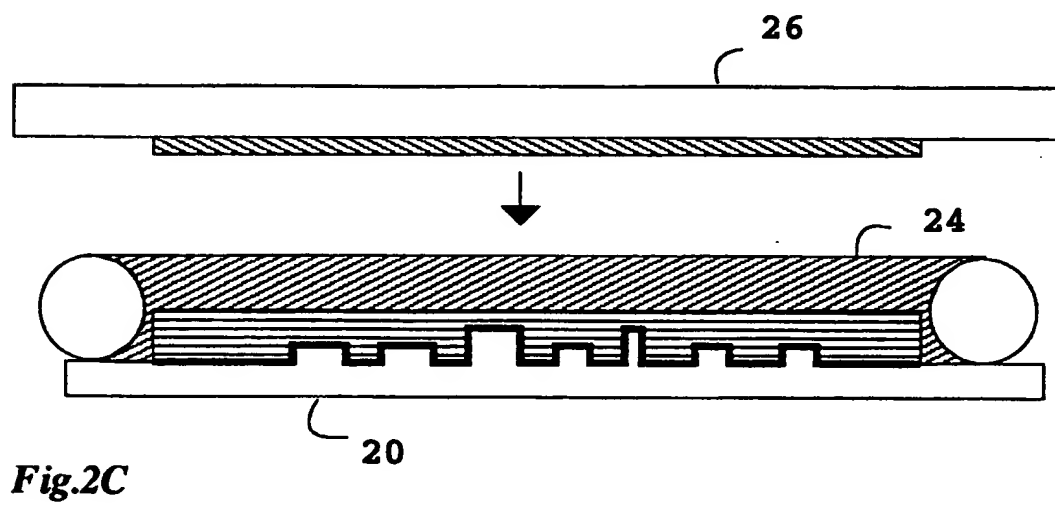
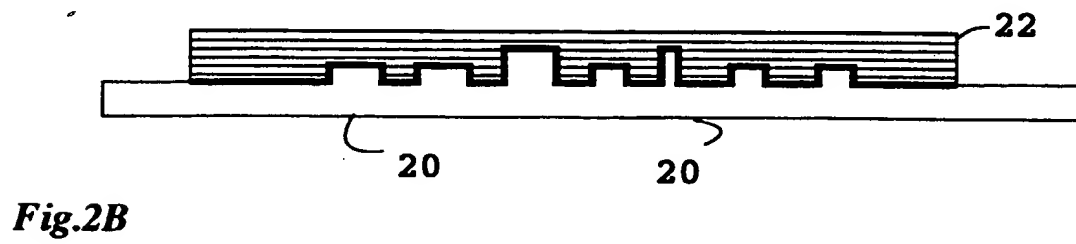
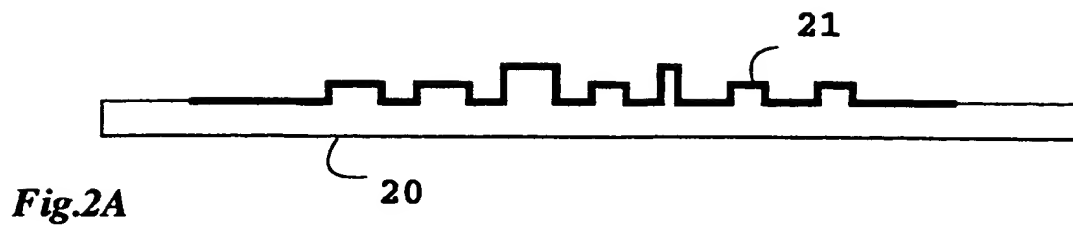
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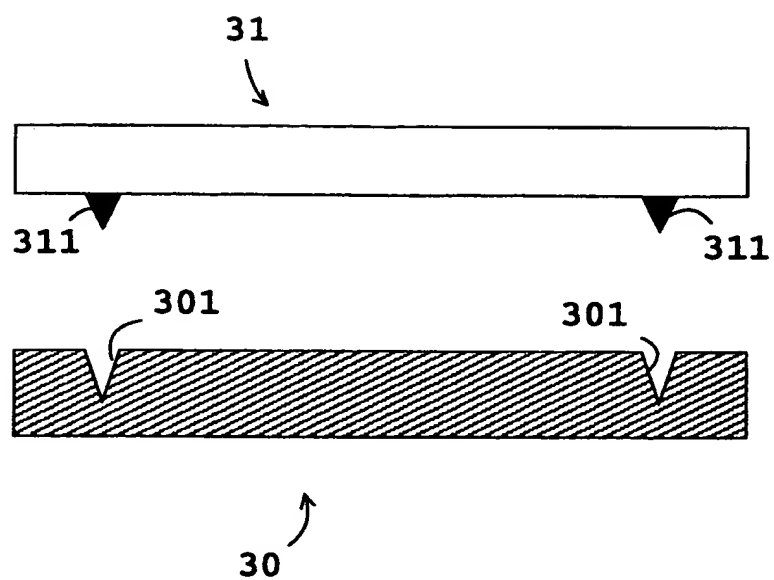
**Fig. 1A****Fig. 1B****Fig. 1C****Fig. 1D**

*Fig. 1E*

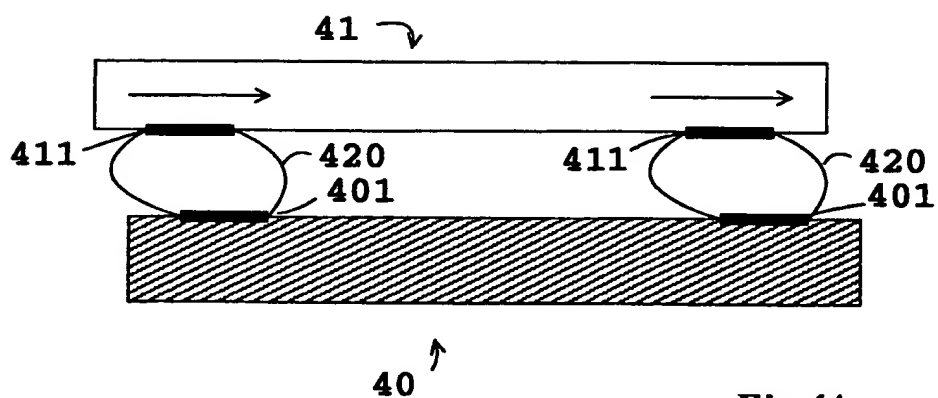
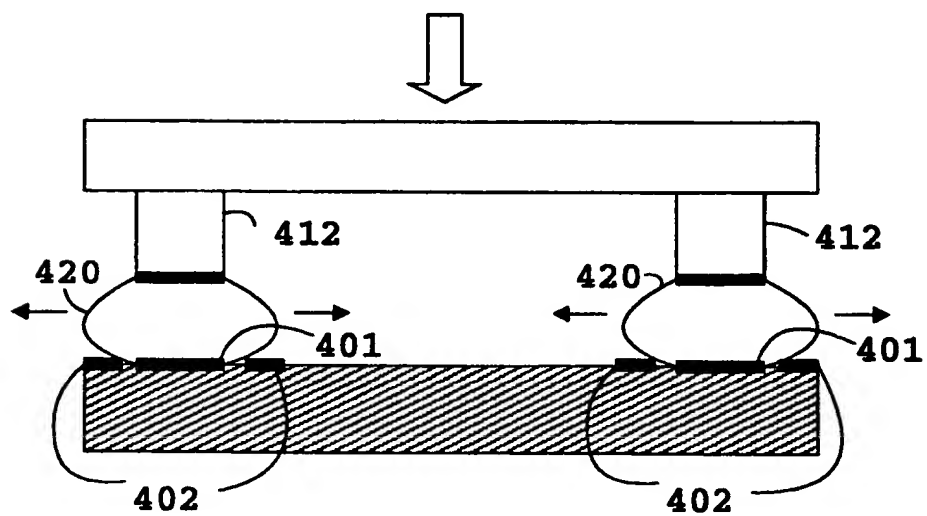
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**Fig.3**

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**Fig.4A****Fig.4B**

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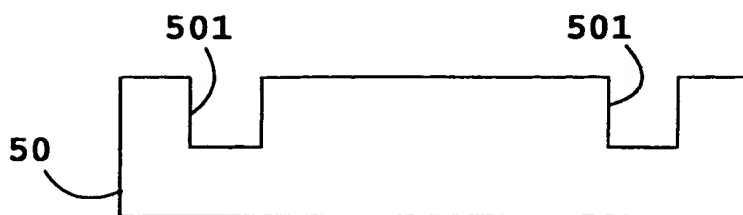


Fig.5

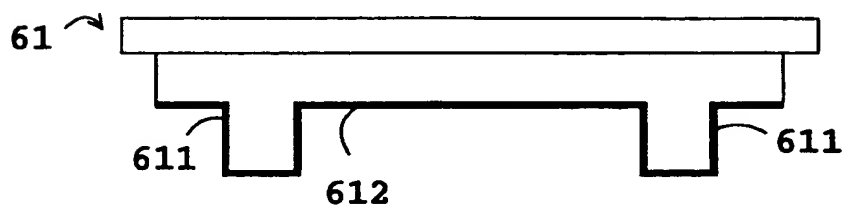


Fig.6A

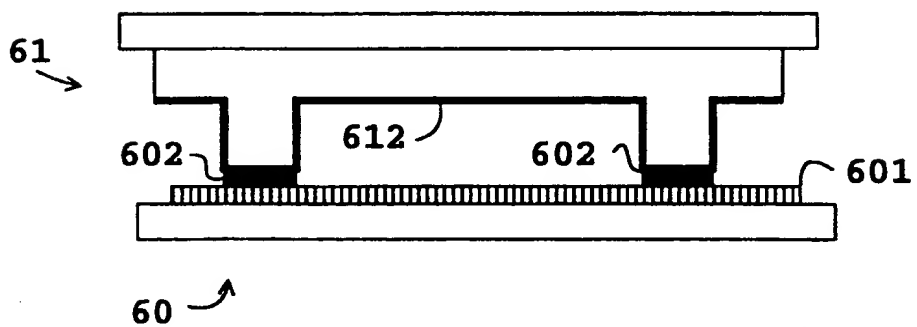


Fig.6B

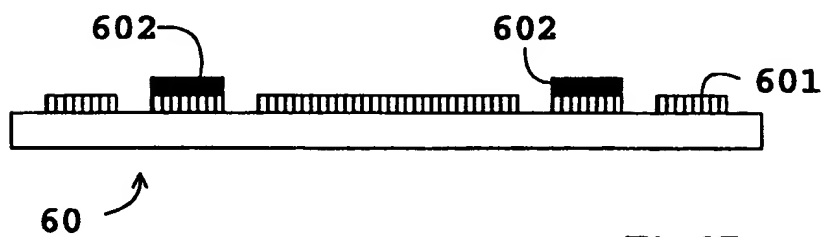


Fig.6C

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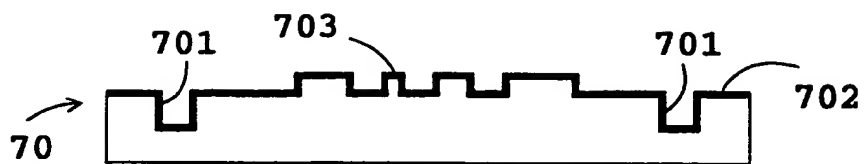


Fig. 7A



Fig. 7B

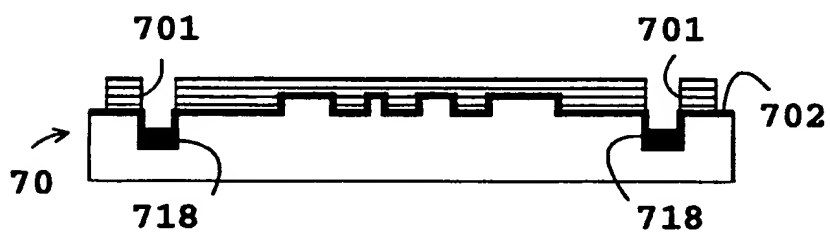


Fig. 7C

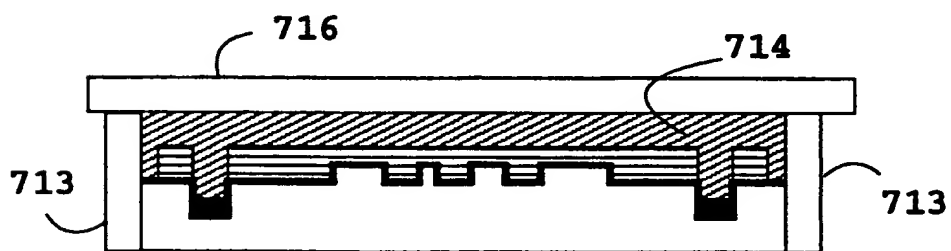


Fig. 7D

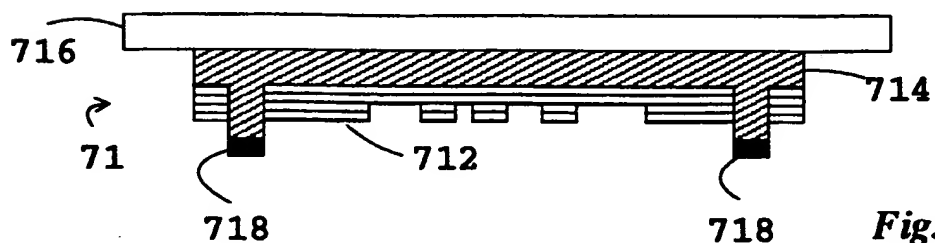


Fig. 7E

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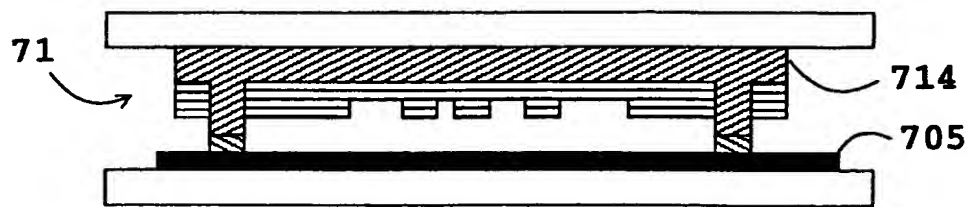


Fig. 7F

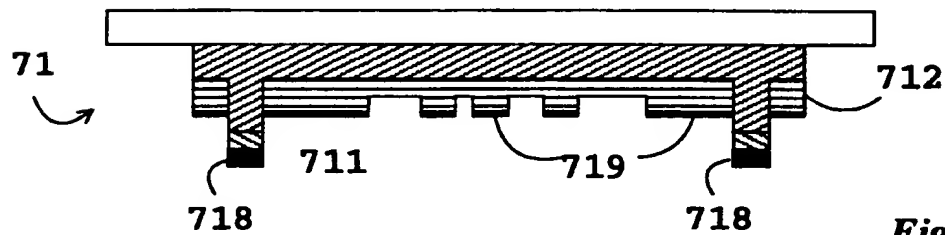


Fig. 7G

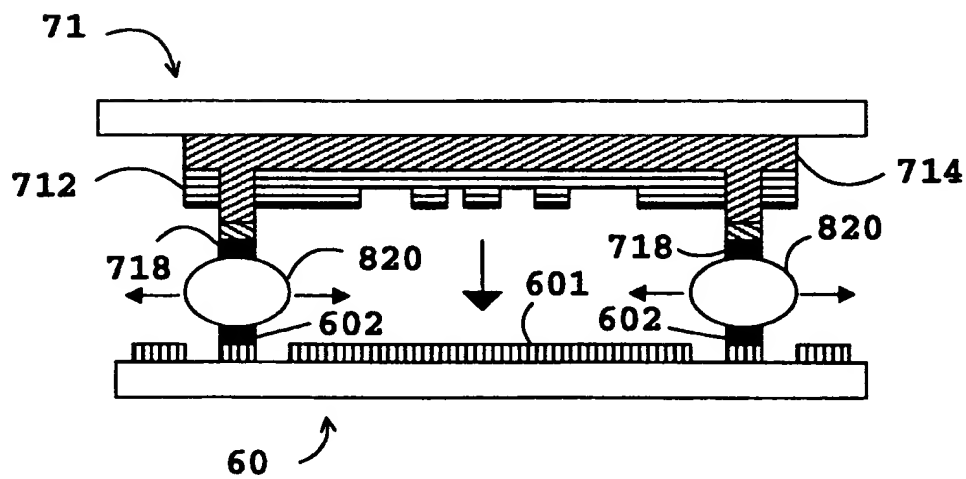


Fig. 8

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 95/00609

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 B41K1/00 G03F7/00 H01L21/768 B41C1/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 B41K G03F H01L B41C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	ADVANCED MATERIALS, vol. 7, no. 5, May 1995, WEINHEIM DE, pages 471-473, XP000533523 Y. XIA ET AL.: "Reduction of Size of Features of Patterned SAMs Generated by Microcontact Printing with Mechanical Compression of the Stamp" see the whole document ---	1-9
Y	FR,A,2 663 760 (AMRI DAHBIA) 27 December 1991 see page 2, line 3 - line 6 ---	1-9
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">26 April 1996</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">07.06.96</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Rasschaert, A</div>

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 95/00609

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 26, no. 11, April 1994, NEW YORK US, pages 5993-5994, XP002001687 M.J. BRADY ET AL.: "Self-aligned Optical Fiber/Laser Structure" see the whole document ---	4
Y	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 29, no. 2, July 1986, NEW YORK US, pages 560-562, XP002001688 "Method for Assembling a multilayer planar object" see the whole document ---	4
A	EP,A,0 583 714 (DU PONT) 23 February 1994 see the whole document ---	1
A	ADVANCED MATERIALS, vol. 7, no. 7, July 1995, WEINHEIM DE, pages 649-652, XP000520481 J.WILBUR ET AL.: "Lithographic Molding : A convenient Route to Structures with Sub_Micron Dimensions" see the whole document ---	1-9
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